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FORMATION AND STRUCTURE OF Al(PO<sub>3</sub>)<sub>3</sub> SYSTEM GLASSES, (U)  
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FORMATION AND STRUCTURE OF  $\text{Al}(\text{PO}_3)_3$  SYSTEM GLASSES

by

Fu-xi Gan, Ya-si Jiang, and Fu-song Jiang

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## **EDITED TRANSLATION**

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FORMATION AND STRUCTURE OF AL( $PO_3$ )<sub>3</sub> SYSTEM GLASSES

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### Abstract

In this work we researched glasses with  $\text{Al}(\text{PO}_3)_3$  systems, in particular  $\text{Al}(\text{PO}_3)_3\text{-AlF}_3\text{-kF(kF}_2)$  systems. We have determined the glass formation regions of  $\text{Al}(\text{PO}_3)_3\text{-RF(RF}_2)$  and  $\text{Al}(\text{PO}_3)_3\text{-AlF}_3\text{-RF-RF}_2$  systems, and by using the methods of differential thermal analysis, X-ray diffraction analysis, and infrared spectroscopy, we have identified the structural units of devitrification products within these glasses. We also discuss the structures of these glasses in the present work.

When fluorides are introduced into metaphosphate glass, this will cause the long  $[\text{PO}_4]$  chains to break. The length of the chains is shortened as the fluoride content is increased, and the glass gradually changes into a pyrophosphate structure. Meanwhile, with the presence of alkali fluorides,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Li}^+$  ions can form  $[\text{AlF}_4]$ ,  $[\text{MgF}_4]$ , and  $[\text{LiF}_4]$  structural units respectively, which link up the broken chains. On the other hand,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  all act as glass network modifying ions.

## 1. Foreword

Fluorophosphate glass systems have good optical qualities: their refraction ratios are low, their aperture numbers are large; they are optical glasses with low chromatic dispersion. Since they still have special relative portions of chromatic dispersion, they are optical glasses with special chromatic dispersion. In a few optical systems with the second degree spectrum removed, one can use fluorophosphate glass and other fluorophosphates to match each other, and obtain redispersed chromatism within a broad spectral range. Fluorophosphate glasses also have low nonlinear refraction ratios, and reduce deterioration in quality and focusing phenomena that occur with light beams under the effect of strong light. They are the basic glasses for laser work materials produced in high power laser beam systems. From the 1950's to the 1960's, since optical glasses were first developed, every nation has conducted some research on them and has manufactured some practical optical glasses. In order to meet the need for high power laser equipment, some practical research on optical glasses was pursued once again in the 1970's. At the same time that fluorophosphate glasses were being produced, there had already been some research done on the production, characteristics, and structure of these glasses, but they were still little understood in comparison with silicate, borate, and phosphate glasses. Because of this, research on fluorophosphate glasses is of both theoretical and practical interest.

In light of the structural similarity between  $\text{BeF}_2$  and  $\text{SiO}_2$ , G. Heyne<sup>(1)</sup> did research using  $\text{BeF}_2$  as the basic fluoride glass.

This type of glass remains open to investigation concerning its physical and chemical properties, as well as its manufacturing techniques. With the introduction of metaphosphates into glass, a fluoride glass containing phosphates is produced, which gradually turns into a fluorophosphate glass not containing  $\text{BeF}_2$ . Fluorophosphate glasses are divided into three systems, according to the differences in their metaphosphate content: the  $\text{NaPO}_3$  system, the  $\text{Ba}(\text{PO}_3)_2$  system, and the  $\text{Al}(\text{PO}_3)_3$  system. Pei-zhen Deng<sup>(2)</sup> has carefully researched the  $\text{NaPO}_3$  system, M.L. Petrovskaya<sup>(3)</sup>, A.A. Pronkin<sup>(4)</sup> et al. have researched the  $\text{Ba}(\text{PO}_3)_3$  system's characteristics and structure, and L.N. Urusovskaya<sup>(5)</sup>, L.A. Golubtsov<sup>(6)</sup>, A.A. Pronkin et al. have researched the  $\text{Al}(\text{PO}_3)_3\text{-R}$  two-component glass system and the  $\text{Al}(\text{PO}_3)_3\text{-BaF}_2\text{-RF}$  three-component glass system. While fluorophosphate laser glasses were being researched, there were also people trying to determine the formation of  $\text{Al}(\text{PO}_3)_3\text{-AlF}_3\text{-RF}_3\text{-RF-KF}_2$  glass systems and the characteristics of the individual glasses.

On the basis of our total knowledge of the properties of inorganic glasses, we believe that  $\text{AlF}_3$  is one of the major ingredients of fluorophosphate glasses, and that it handles the effects of intermediate chemical compounds in fluorophosphate glasses. The present work discusses fluorophosphate glasses that have  $\text{Al}(\text{PO}_3)_3$  as a base, with emphasis on  $\text{AlF}_3$ -containing glasses, and identifies the glasses' formation regions. We used the methods of infrared spectroscopy, differential thermal analysis, and X-ray diffraction analysis to conduct research on glass and devitrified samples, in order to gain an understanding of the negative ion radicals present in the glass. Relating this to the formation regions of glasses, we discuss

the structure of fluorophosphate glasses, and put forth a fairly definite point of view.

## 2. The Glass Formation Regions

The glass formation regions of the  $\text{Al}(\text{PO}_3)_3\text{-RF}(\text{RF}_2)(\text{RF}_3)$  two-component system and of the  $\text{Al}(\text{PO}_3)_3\text{-AlF}_3\text{-RF}_2\text{-RF}$  four-component system have been determined. The raw materials used were: experimental reagent  $\text{Al}(\text{PO}_3)_3$  and chemically pure fluoride. They were melted in a platinum crucible, with 20 g. of glass used each time to melt in the experiment. After mixing, it was poured into an iron mold and allowed to cool naturally in the open air. The glass formation regions of the two-component system are listed in Table 1, and for the glass formation regions of the four-component system, see Figs. 1 and 2.

As fluorophosphate glasses are melted, the fluorine has a definite volatilization. We selected a certain number of glass samples and did a chemical analysis of their total fluorine content. The results indicated that in glasses with high fluoride content, most of the fluorine was volatized in the form of fluorine oxide, and the change in the fluorine to oxygen ratio in the glass is not great.

Table 1. Glass formation regions of the  $\text{Al}(\text{PO}_3)_3\text{-RF}_x$  two-component system glasses

glass system	RF <sub>x</sub> content (mol%)
$\text{Al}(\text{PO}_3)_3\text{-LiF}$	79~85
$\text{Al}(\text{PO}_3)_3\text{-NaF}$	72~81
$\text{Al}(\text{PO}_3)_3\text{-KF}$	66~78
$\text{Al}(\text{PO}_3)_3\text{-SrF}_2$	0~35
$\text{Al}(\text{PO}_3)_3\text{-BaF}_2$	66~74
$\text{Al}(\text{PO}_3)_3\text{-AlF}_3$	0~25

As the melted mass cools, the glass often becomes devitrified, and the devitrified grains are very small; with the naked eye or an optical microscope it is difficult to distinguish whether they are separate crystals or phase splittings. We used an electric scanning scope to investigate this; cf. Fig. 3(1) for the appearance of the devitrified grains. In the glasses with relatively high  $\text{AlF}_3$  and  $\text{RF}_2$  content, the glass devitrification was rather strong, and belonged to the split phase class (cf. Fig. 3(1)). In the glasses with relatively high RF content, the devitrification was lumped, and appeared in the form of separate crystals (cf. Fig. 3(4)). Most of the glasses eventually produced phase splittings and separate crystals.

From the above-mentioned glass formations we can see that: 1) in the regions of high fluoride content in  $\text{Al}(\text{PO}_3)_3\text{-RF}$  systems, the amount of LiF absorbed was greatest, and the KF was least. In  $\text{Al}(\text{PO}_3)_3\text{-AlF}_3$  systems that did not contain RF or  $\text{RF}_2$ , the high-fluoride regions did not form glass. 2) In the four-component systems where  $\text{Al}(\text{PO}_3)_3=15 \text{ mol\%}$ , when  $\text{AlF}_3=0$ , it was only the systems containing LiF or  $\text{MgF}_2$  that formed glass. 3) In the four-component systems that only contained NaF, KF,  $\text{CaF}_2$ ,  $\text{SrF}_2$ , or  $\text{BaF}_2$ , glass could form only if the system contained  $\text{AlF}_3$ , regardless of whether  $\text{Al}(\text{PO}_3)_3=10 \text{ mol\%}$  or  $\text{Al}(\text{PO}_3)_3=15 \text{ mol\%}$ .

According to the research on inorganic glass structure<sup>(9)</sup>, glass formation and network structures not dependent upon glass have the following property: that devitrification of glass and destruction of networks are related to the formation of networks of different qualities, and moreover, can be classified as accumulation regions and destruction regions on the basis of their degree of joining. In dif-

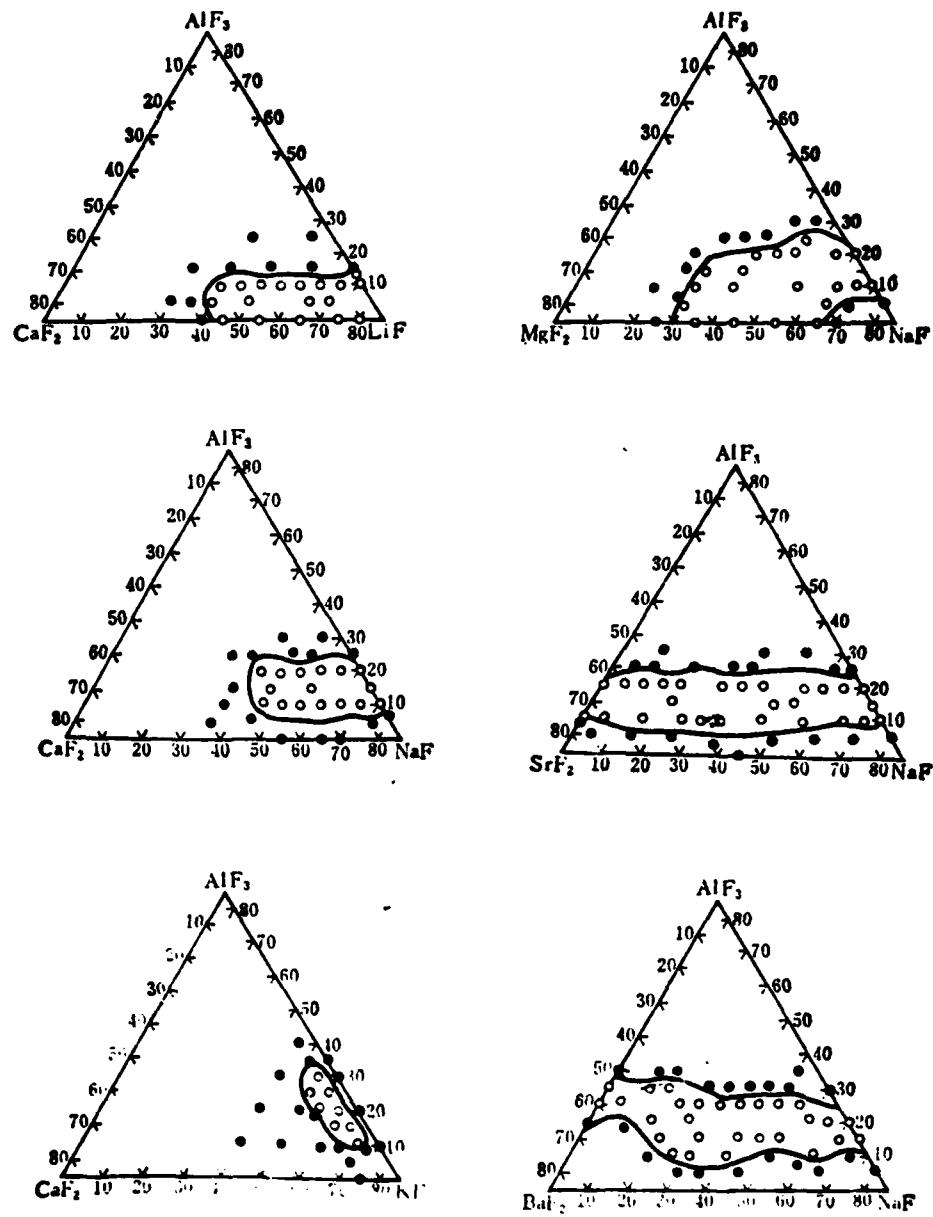


Fig. 1. The glass formation regions of  $\text{Al}(\text{PO}_3)_3$ - $\text{AlF}_3$ -RF- $\text{RF}$  four-component systems when  $\text{Al}(\text{PO}_3)_3$  content is 15 mol%.

-- transparent glass

●-- devitrification

ferent regions, each type of glass component differs with respect to the influence of devitrification. In the present work, in regions with low  $\text{Al}(\text{PO}_3)_3$  content, the networks of glass formation suffered a great deal of destruction, located in the destruction regions. The influence of the introduction of a given component on glass formation is dependent on its ability to destroy networks or to cause already destroyed networks to join back together.

From the above-mentioned glass formation regions it can be seen that the introduction of  $\text{AlF}_3$  can cause glass formation regions to expand. If  $\text{Al}(\text{PO}_3)_3=10 \text{ mol\%}$  or  $15 \text{ mol\%}$ ,  $\text{Al}(\text{PO}_3)_3-\text{CaF}_2-\text{NaF}$ ,  $\text{Al}(\text{PO}_3)_3-\text{SrF}_2-\text{NaF}$ , and  $\text{Al}(\text{PO}_3)_3-\text{CaF}_2-\text{KF}$  can all form glass with the introduction of  $\text{AlF}_3$ . It can be said that under the condition that  $\text{KF}$  or  $\text{KF}_2$  content is present,  $\text{AlF}_3$  causes networks that have suffered great destruction to join together again, if the  $\text{Al}(\text{PO}_3)_3$  content is low.  $\text{AlF}_3$  can also cause glass to form, or cause glass formation regions to expand.  $\text{LiF}$  and  $\text{MgF}_2$  have similar effects, and under the condition that no  $\text{AlF}_3$  content is present, can cause destroyed networks to join together again, and cause glass formation. As far as glass formation is concerned, we believe that in fluorophosphate glasses,  $\text{AlF}_3$ ,  $\text{MgF}_2$ , and  $\text{LiF}$  have the effect of making broken networks join back together.

### 3. Separate Crystals of Glass and Their Resulting Structures

The present work researched three sets of separate crystals of glass: metaphosphates, fluorophosphate glasses with high  $\text{Al}(\text{PO}_3)_3$  content, and fluorophosphate glasses with low  $\text{Al}(\text{PO}_3)_3$  content. The chemical ingredients of each glass were (in mol%):

- 1)  $\text{LiPO}_3$ ; 2)  $\text{Sr}(\text{PO}_3)_2$ ; 3)  $\text{Al}(\text{PO}_3)_3$ ; 4)  $70\text{Al}(\text{PO}_3)_3 \cdot 30\text{SrF}_2$ ;
- 5)  $80\text{Al}(\text{PO}_3)_3 \cdot 20\text{AlF}_3$ ; 6)  $20\text{Al}(\text{PO}_3)_3 \cdot 80\text{LiF}$ ; 7)  $10\text{Al}(\text{PO}_3)_3 \cdot 20\text{AlF}_3 \cdot 50\text{SrF}_2 \cdot 20\text{LiF}$ .

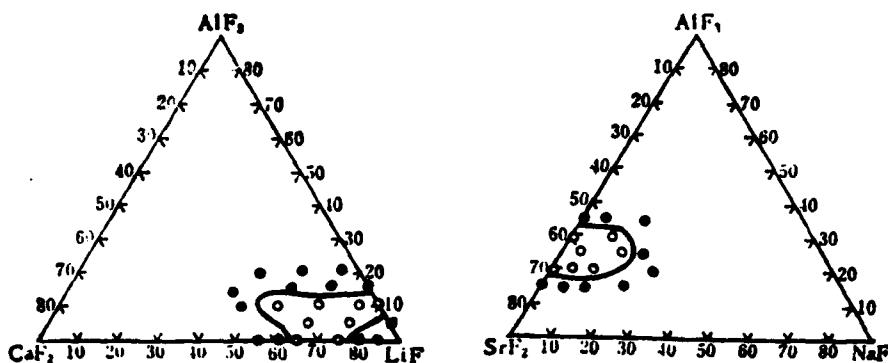


Fig. 2. The glass formation regions of  $\text{Al}(\text{PO}_3)_3$ - $\text{AlF}_3$ -RF<sub>2</sub>-RF four-component systems when  $\text{Al}(\text{PO}_3)_3$  content is 10 mol%.

In the differential thermal curves of each of the above-mentioned glasses, the speed of heat increase was 5 C.<sup>o</sup>/min. at the time of determination, with the results as shown in Fig. 4. The exothermic peak in the differential thermal curve corresponds to the separate crystallization of the glass, and the heat absorption peak corresponds to the melting that led to the separation into crystals. From the figure it can be seen that in single component glasses, the differential thermal curve is comparatively simple, with the exothermic and heat absorption curves fairly obvious. This indicates that only one kind of crystal is separated out. The heat absorption peak of the differential thermal curve is approximately the same as the melting point of the corresponding crystal. The differential thermal curve of glasses with low  $\text{Al}(\text{PO}_3)_3$  content is complex, as with  $20\text{Al}(\text{PO}_3)_3 \cdot 80\text{LiF}$  and  $10\text{Al}(\text{PO}_3)_3 \cdot 20\text{AlF}_3 \cdot 50\text{SrF}_2 \cdot 20\text{LiF}$  glasses. With the former glass two similar exothermic peaks appear,

which indicates that the eventual separation into crystals was different, but they melted at similar temperatures. With the latter glass there existed a strong exothermic peak and several heat absorption peaks, which indicated that it separated into crystals at about 530°C., but there were different melting temperatures. This is approximately the same as the results obtained by X-ray diffraction analysis, to be presented below.

Each type of glass was maintained at around crystallization temperature 12-24 h, and after applying thermal treatment to the samples we used the method of powder X-ray diffraction analysis to determine the diffraction spectrum, and compared it with the standard spectrum in order to determine the result of separation into crystals. The X-ray diffractions of several types of samples are shown in Fig. 5. After analyzing the results, we arrived at the judgment that after thermal treatment, the result of each glass sample's separation into crystals was as shown in Table 2.

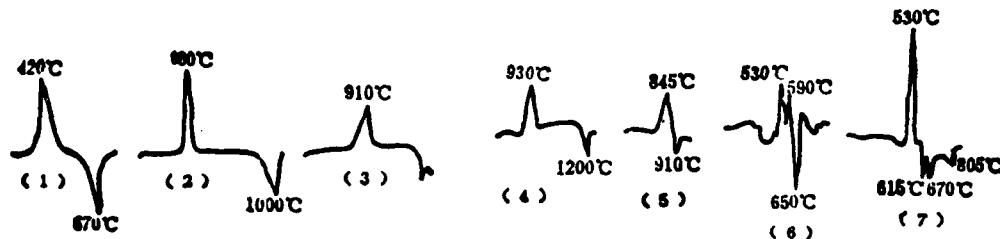


Fig. 4. The differential thermal curves of each type of glass.

- 1)  $\text{LiPO}_4$ ; 2)  $\text{Sr}(\text{PO}_3)_2$ ; 3)  $\text{Al}(\text{PO}_3)_3$ ; 4)  $70\text{Al}(\text{PO}_3)_3 \cdot 30\text{SrF}_2$ ;  
5)  $80\text{Al}(\text{PO}_3)_3 \cdot 20\text{AlF}_3$ ; 6)  $20\text{Al}(\text{PO}_3)_3 \cdot 80\text{LiF}$ ; 7)  $10\text{Al}(\text{PO}_3)_3 \cdot 20\text{AlF}_3 \cdot 50\text{SrF}_2 \cdot 20\text{LiF}$ .

In Table 2 it can be seen that for glasses with a high content of pure metaphosphate or  $\text{Al}(\text{PO}_3)_3$ , the principal crystallization product is metaphosphate. In the portion with low  $\text{Al}(\text{PO}_3)_3$  content, the principal crystallization product is pyrophosphate or aluminum fluoride and aluminum metaphosphate.

In order to understand the various types of structural units involved in crystallization, we used infrared spectroscopy on the samples before and after thermal treatment, and used the method of KBr extrusion tablets to prepare the samples. The infrared spectroscopy results of 7 types of samples before and after thermal treatment are shown in Figure 6.

In the infrared spectroscopy of each metaphosphate glass after thermal treatment, it was found that the extended vibrations produced by the chain structure of the metaphosphate units deform the vibration frequency. For example, with  $\text{LiPO}_3$ , the heat absorption peaks are divided into  $1290 \text{ cm}^{-1}$  ( $\nu_{\text{as}} \text{ PO}_2$ ),  $1150 \text{ cm}^{-1}$  ( $\delta \text{ PO}_2$ ), and approximately  $410 \text{ cm}^{-1}$  ( $\delta \text{ PO}_4$ ). Similarly,  $\text{Sr}(\text{PO}_3)_2$  and  $\text{Al}(\text{PO}_3)_3$  often have changes in the values of peak wavelength and strength.

In  $80\text{Al}(\text{PO}_3)_3$   $20\text{AlF}_3$  and  $70\text{Al}(\text{PO}_3)_3$   $30\text{SrF}_2$ , two types of glass with high  $\text{Al}(\text{PO}_3)_3$  content, the primary crystallization product is  $\text{Al}(\text{PO}_3)_3$ . By comparing the infrared spectroscopy results, it can be ascertained that they are basically similar to  $\text{Al}(\text{PO}_3)_3$ .

In the four-component system glass  $20\text{Al}(\text{PO}_3)_3$   $80\text{LiF}$  with  $\text{Al}(\text{PO}_3)_3=10 \text{ mol\%}$ , the  $\text{Al}(\text{PO}_3)_3$  content is low, and the special feature of the infrared spectroscopy results of thermally treated samples is that  $1260-1300 \text{ cm}^{-1}$  does not exist in the characteristic absorption peak of the metaphosphate structures, which instead have

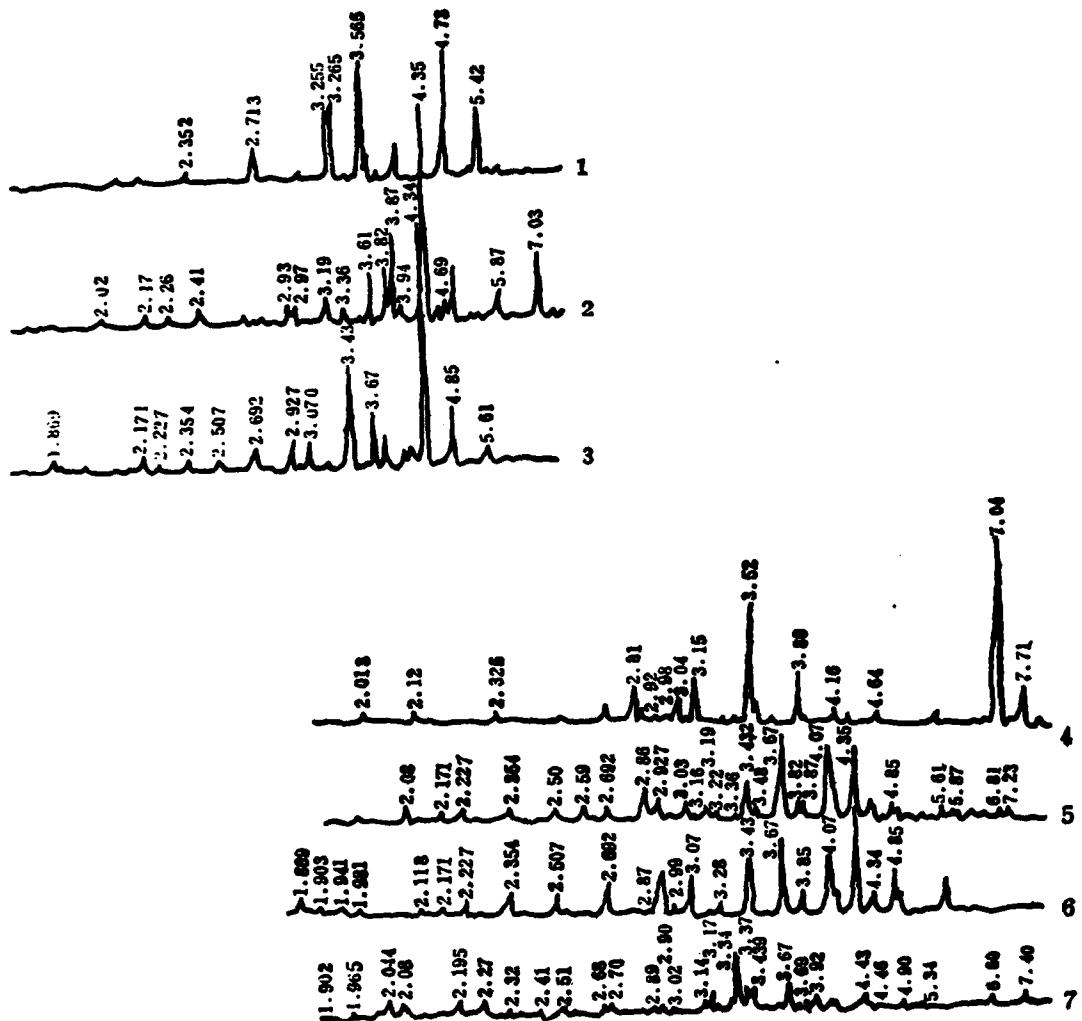


Fig. 5. The X-ray graphs of thermally treated samples.

1-LiPO<sub>3</sub>; 2-Sr(PO<sub>3</sub>)<sub>2</sub>; 3-Al(PO<sub>3</sub>)<sub>3</sub>; 4-20Al(PO<sub>3</sub>)<sub>3</sub>·80LiF, 535 °C., 12h;  
5-70Al(PO<sub>3</sub>)<sub>3</sub>·20AlF<sub>3</sub>, 1100 °C., 12h; 7-10Al(PO<sub>3</sub>)<sub>3</sub>·20AlF<sub>3</sub>·50SrF<sub>2</sub>·20LiF,  
530 °C., 12h.

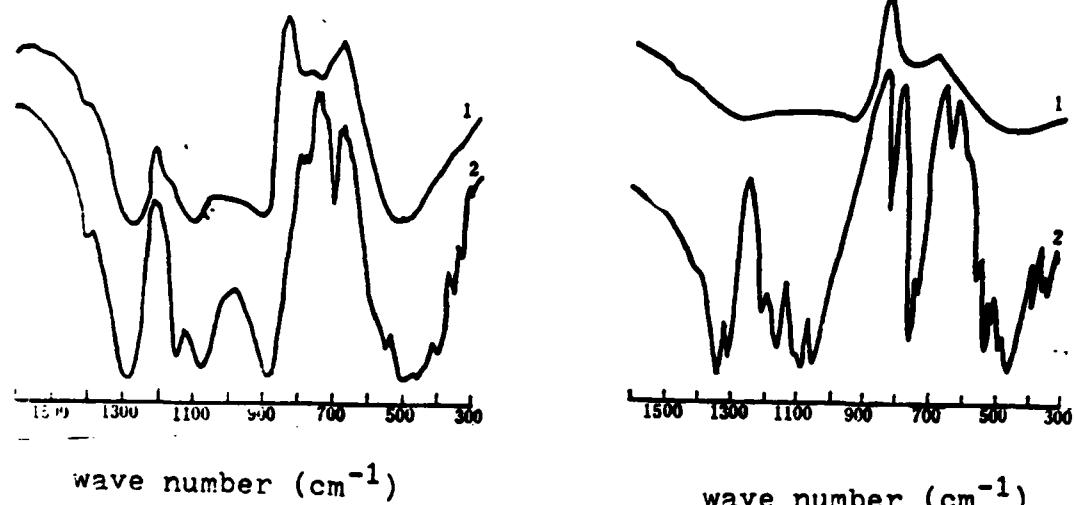


Fig. 6(1). The infrared spectra of  $\text{LiPO}_3$  samples before and after thermal treatment.

1- $\text{LiPO}_3$  glass; 2- $\text{LiPO}_3$ , 420°C., 24h

wave number (cm<sup>-1</sup>)

Fig. 6(2). The infrared spectra of  $\text{Sr}(\text{PO}_3)_2$  samples before and after thermal treatment.

1- $\text{Sr}(\text{PO}_3)_2$  glass; 2- $\text{Sr}(\text{PO}_3)_2$ , 600°C., 24h

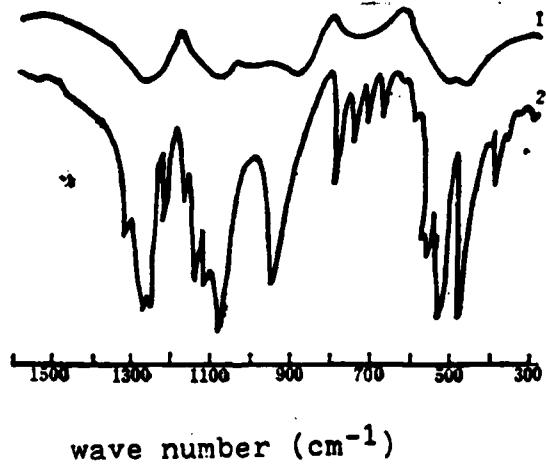


Fig. 6(3). The infrared spectra of  $\text{Al}(\text{PO}_3)_3$  samples before and after thermal treatment.

1- $\text{Al}(\text{PO}_3)_3$  glass; 2- $\text{Al}(\text{PO}_3)_3$ , 900°C., 24h

an absorption of  $1100\text{-}1200\text{ cm}^{-1}$  for the characteristic spreading vibrations ( $\nu_{as}\text{ PO}_3$ ) of the pyrophosphates. In  $20\text{Al}(\text{PO}_3)_3\text{-}80\text{LiF}$  samples, absorption of  $1260\text{ cm}^{-1}$  indicates that there still remain small amounts of metaphosphate radicals. The absorption peak of  $545\text{ cm}^{-1}$  obtained with thermal treatment samples, according to A.A. Pronkin<sup>(7)</sup> belongs to the vibrations of  $\text{AlF}_6^{3-}$ . The infrared spectroscopy results of thermally treated samples of four-component systems basically correspond to  $\text{Sr}_2\text{P}_2\text{O}_7$ . Each absorption peak is distinguished by the pyrophosphate system's spreading vibrations and deformed vibrations. They are  $1190\text{ cm}^{-1}$ ,  $1140\text{ cm}^{-1}$ ,  $1110\text{ cm}^{-1}$  ( $\nu_{as}\text{ PO}_3$ ),  $1050\text{ cm}^{-1}$ ,  $1015\text{ cm}^{-1}$ ,  $980\text{ cm}^{-1}$  ( $\nu_{g\text{-}}\text{PO}_3$ ),  $750\text{ cm}^{-1}$  ( $\nu_{g\text{-}}\text{POP}$ ),  $565\text{ cm}^{-1}$ ,  $550\text{ cm}^{-1}$  ( $\nu_{as}\text{ PO}_3$ ),  $550\text{ cm}^{-1}$ ,  $490\text{ cm}^{-1}$  ( $\delta\text{, PO}_3$ ). Because of this, it is ascertainable that the basic structural units are pyrophosphate structures.

Table 2. Crystallization products of each glass sample after thermal treatment

Glass	Major crystal-	Other crystal-
	lization	lization
LiPO <sub>4</sub>	LiPO <sub>4</sub>	
Sr(PO <sub>4</sub> ) <sub>2</sub>	Sr(PO <sub>4</sub> ) <sub>2</sub>	
Al(PO <sub>4</sub> ) <sub>3</sub>	Al(PO <sub>4</sub> ) <sub>3</sub>	
80Al(PO <sub>4</sub> ) <sub>3</sub> -20AlF <sub>6</sub>	Al(PO <sub>4</sub> ) <sub>3</sub>	AlPO <sub>4</sub>
70Al(PO <sub>4</sub> ) <sub>3</sub> -30SrF <sub>6</sub>	Al(PO <sub>4</sub> ) <sub>3</sub>	$\alpha$ -Sr(PO <sub>4</sub> ) <sub>2</sub> $\beta$ -Sr(PO <sub>4</sub> ) <sub>2</sub>
20Al(PO <sub>4</sub> ) <sub>3</sub> -80LiF	AlF <sub>6</sub> , Li <sub>2</sub> PO <sub>4</sub>	AlPO <sub>4</sub> , LiF
10Al(PO <sub>4</sub> ) <sub>3</sub> -20AlF <sub>6</sub> - 50SrF <sub>6</sub> -30LiF	$\alpha$ -Sr <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	$\alpha$ -Sr(PO <sub>4</sub> ) <sub>2</sub>

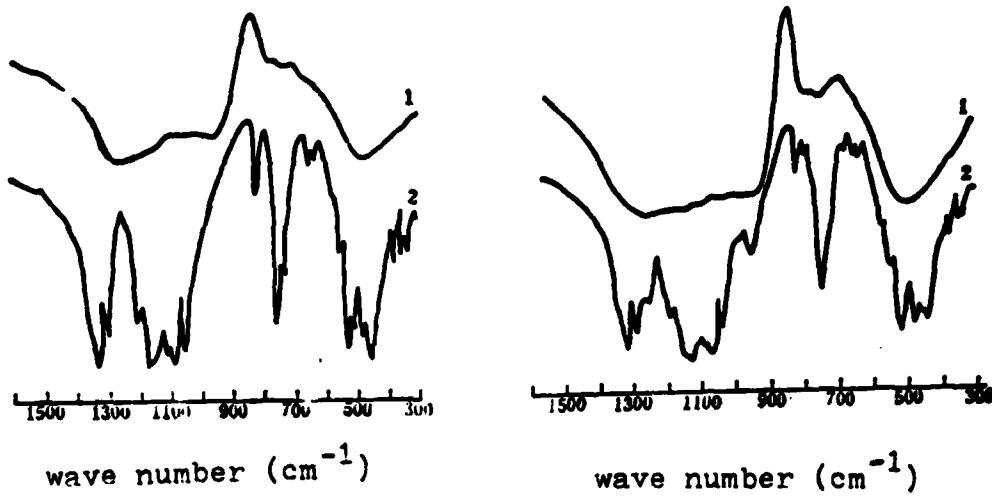


Fig. 6(4). Infrared spectra of  $80\text{Al}(\text{PO}_3)_3 \cdot 20\text{AlF}_3$  samples before and after thermal treatment.

1- $80\text{Al}(\text{PO}_3)_3 \cdot 20\text{AlF}_3$  glass;  
2- $80\text{Al}(\text{PO}_3)_3 \cdot 20\text{AlF}_3$ ,  
1100°C., 12h.

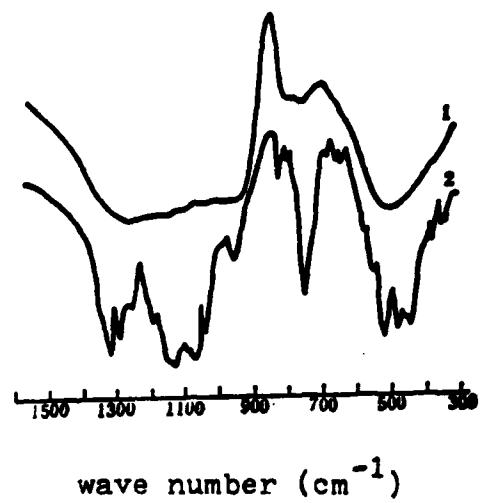


Fig. 6(5). Infrared spectra of  $70\text{Al}(\text{PO}_3)_3 \cdot 30\text{SrF}_2$  samples before and after thermal treatment.

1- $70\text{Al}(\text{PO}_3)_3 \cdot 30\text{SrF}_2$  glass;  
2- $70\text{Al}(\text{PO}_3)_3 \cdot 30\text{SrF}_2$ , 845°C.,  
12h.

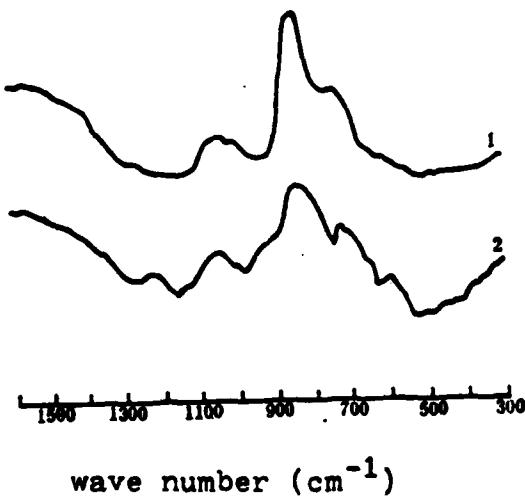


Fig. 6(6). Spectra of  $20\text{Al}(\text{PO}_3)_3 \cdot 80\text{LiF}$  samples before and after thermal treatment.

1- $20\text{Al}(\text{PO}_3)_3 \cdot 80\text{LiF}$  glass;  
2- $20\text{Al}(\text{PO}_3)_3 \cdot 80\text{LiF}$ , 535°C.,  
12h

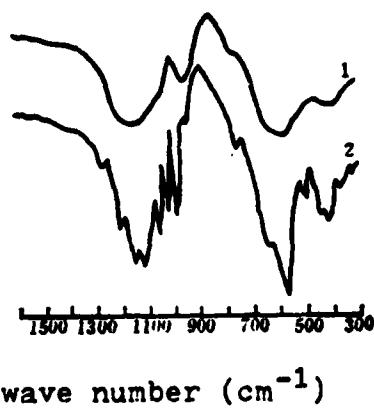


Fig. 6(7). Spectra of  $10\text{Al}(\text{PO}_3)_3 \cdot 20\text{AlF}_3 \cdot 50\text{SrF}_2 \cdot 20\text{LiF}$  samples before and after thermal treatment.

1- $10\text{Al}(\text{PO}_3)_3 \cdot 20\text{AlF}_3 \cdot 50\text{SrF}_2 \cdot 20\text{LiF}$  glass;  
2- $10\text{Al}(\text{PO}_3)_3 \cdot 20\text{AlF}_3 \cdot 50\text{SrF}_2 \cdot 20\text{LiF}$ , 530°C., 24h

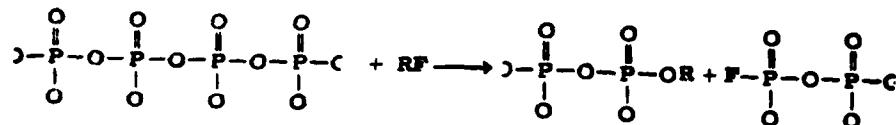
#### 4. The Structure of Fluorophosphate Glasses

Infrared spectrometry is an effective method for conducting research on material structures, and also has extensive applications in research on glass materials. Because we have a comparatively good understanding of crystal structures, we can often compare the infrared spectroscopy results of glasses and crystals, and determine the structure of glasses on the basis of the various structures found in crystals. The infrared spectra of 7 types of glasses are shown in Fig. 6. It can be seen that the infrared spectra of glasses are similar in appearance to the spectral lines of the corresponding thermal treatment samples, but more diffuse. In comparing the infrared spectra of glasses with those of samples after thermal treatment, it can be affirmed that the structure of metaphosphate glasses is similar to that of the corresponding crystals. As crystal changes into glass, the basic structural units are preserved. For fluorophosphate glasses with high  $\text{Al}(\text{PO}_3)_3$  content, the infrared spectrum is similar to that of  $\text{Al}(\text{PO}_3)_3$ , and the metaphosphate structure is maintained. For glasses with low  $\text{Al}(\text{PO}_3)_3$  content, the basic structural units are pyrophosphate radicals. As the fluoride content is increased,  $[\text{PO}_3\text{F}]^{2-}$  structures still appear, and their infrared spectral lines overlap with those of the metaphosphates.

The products of fluorophosphate glasses are not metaphosphates, and the structure of fluorophosphate glasses has been researched<sup>[9,10]</sup>. Metaphosphate glasses have a long chain structure compound of  $[\text{PC}_4]$  four-sided radicals, and the network modifying ions fill the gaps in the chain. In discussing the structure of fluorophosphate

glasses, it is necessary to begin with the structure of the metaphosphates.

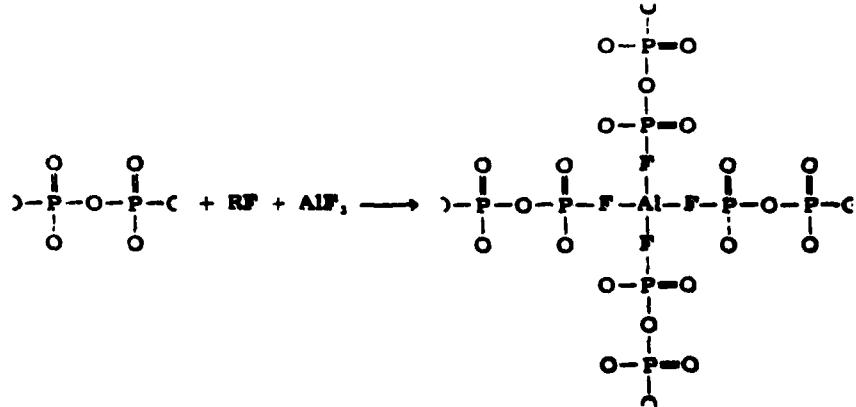
The addition of fluoride to metaphosphates is like the addition of network modifying bodies to oxide glasses; the  $\text{PO}_4$  phosphorus-oxygen chain breaks, and assumes the form of a  $\text{PO}_3\text{F}$  four-sided body, and the  $\text{PO}_3\text{F}$  becomes the terminal of a long chain. According to the increase of fluoride introduced, the length of the chain continually decreases. For instance, the addition of the alkali fluoride RF changes the course of events as follows.



Additionally, the network structure gradually breaks, shortens, and turns into a pyrophosphate structure. In glasses with high  $\text{Al}(\text{PO}_3)_3$  content, like the  $80\text{Al}(\text{PO}_3)_3 20\text{AlF}_3$  and  $70\text{Al}(\text{PO}_3)_3 30\text{SrF}_2$  glasses, the structural network of metaphosphate radicals is basically preserved. In glasses with low  $\text{Al}(\text{PO}_3)_3$  content, such as  $20\text{Al}(\text{PO}_3)_3 80\text{LiF}$  and  $10\text{Al}(\text{PO}_3)_3 20\text{AlF}_3 50\text{SrF}_2 20\text{LiF}$ , the basic structures turn into pyrophosphate radical structures. This process of changing can be seen clearly in the infrared spectra. For this reason, the special characteristic of fluorophosphate glasses is that they take the form of  $[\text{PO}_3\text{F}]^{2-}$  with the continuous addition of fluoride. Also, the long metaphosphate chains shorten, and the glasses gradually turn into pyrophosphate structural networks.

Rather special components in fluorophosphate glasses are  $\text{AlF}_3$ ,  $\text{MgF}_2$ , and  $\text{LiF}$ . From research on silicates, borates, and phosphates it is known that for ions of relatively small radius, when there

are alkaline metals or alkaline-earth metals present, they can take the form of the corresponding negative ion four-sided body and enter the glass network. In silicate glasses, every positive ion's structural condition has a significant relation to the radius ratio of positive ions and oxygen ions. In the same way, in fluorophosphate glasses, the radius ratios of the positive ions and fluorine ions has a very great influence on the glass' structure. According to the size of the radius ratios between negative and positive ions, each fluoride and oxide has correspondingly similar structural patterns. (E.g.,  $\text{BeF}_2\text{-SiO}_2$ ,  $\text{LiF-MgO}$ ,  $\text{NaF-CaO}$ ,  $\text{MgF}_2\text{-TiO}_2$ ,  $\text{AlF}_3\text{-MoO}_3$ .) The structural form and characteristics of each fluoride within glass can be compared with the oxides, which have similar patterns. In oxide glasses,  $\text{Mg}^{2+}$ ,  $\text{Ti}^{4+}$ , and  $\text{Mo}^{6+}$  under certain conditions all can take the form of their own four-sided body structures, and enter the glass network in the form of bodies found within glass. Similarly, we believe that in fluorophosphate glasses, when  $\text{xF}$  or  $\text{RF}_2$  is present,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Li}^+$  also can take the form of  $[\text{AlF}_4]$ ,  $[\text{MgF}_4]$ , and  $[\text{LiF}_4]$  four-sided bodies, and cause broken and shortened chains that have  $[\text{PO}_3\text{F}]$  as terminals to join together again, and increase the glass' stability. Taking  $\text{AlF}_3$  as an example, this process can be expressed as follows:



Moreover, when RF is present, then as  $\text{AlF}_3$  is introduced,  $\text{Al}^{3+}$  becomes the center, and  $\text{AlF}_4^-$  takes shape, and causes the  $\text{PO}_3^{\text{F}}$  in the chain's terminal to join back together. It also causes the structure's chains to lengthen, and take the form of a 2-dimensional structural network. The situation for  $\text{MgF}_2$  and  $\text{LiF}$  is similar. From the preceding discussion, it can be seen that for the glass formation regions in  $\text{Al}(\text{PO}_3)_3$ -RF systems, the greatest fluoride content that can be present for glass to form holds for  $\text{LiF}$ . In the above three-component systems, when  $\text{Al}(\text{PO}_3)_3 = 15 \text{ mol\%}$ , the introduction of  $\text{AlF}_3$  causes the glass to stabilize, and in the  $\text{Al}(\text{PO}_3)_3$ - $\text{RF}_2$ -RF systems when  $\text{AlF}_3 = 0$ , glass can form only when  $\text{LiF}$  or  $\text{MgF}_2$  is present; this explains why  $\text{AlF}_3$ ,  $\text{MgF}_2$ , and  $\text{LiF}$  have a joining effect upon networks. Other single valued and dual valued chemicals such as  $\text{NaF}$ ,  $\text{KF}$ ,  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ , belong to the outer part of the network, and themselves cause the long chains of metaphosphate radicals to break. When the fluoride content is high, there exist many fluorine ions in the glass, and the glass' structural chains break severely; at this time the stronger positive ions in the outer part of the network repair the broken fluorine-oxygen chain ends, and possibly have a beneficial effect if preventing devitrification in the glass. This insures that even when there is little glass formation material present, glass can still form.

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